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Accepted Version

Peer-review status of attached file:

Peer-reviewed

Citation for published item:

Moussa, J. and Cheminel, T. and Freeman, G. R. and Chamoreau, L. M. and Williams, J. A. G. and Amouri, H. (2014) 'An unprecedented cyclometallated platinum(II) complex incorporating a phosphinine co-ligand : synthesis and photoluminescence behaviour.', *Dalton transactions.*, 43 (22). pp. 8162-8165.

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An unprecedented cyclometallated platinum(II) complex incorporating a phosphinine co-ligand: synthesis and photoluminescence behaviour[†]

Jamal Moussa,^{a*} Thomas Cheminel,^a Gemma R. Freeman,^b Lise-Marie Chamoreau,^a J. A. Gareth Williams^b and Hani Amouri^{a*}

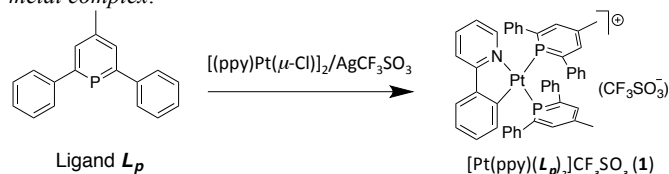
The first luminescent cyclometallated platinum(II) complex bearing phosphinine co-ligands is reported. The long-lived luminescence, which it displays at 77 K, is assigned to a phosphinine-localised triplet excited state on the basis of electrochemical data and TD-DFT calculations.

Cyclometallated Pt(II) complexes have been increasingly studied over the last decade, with a view to applying their attractive luminescence properties in devices such as organic light-emitting diodes.^{1,2} These complexes typically comprise of a cyclometallating ligand – such as 2-phenylpyridine or related aryl-heterocycles – and various co-ligands completing the coordination sphere. Co-ligands frequently used include β -diketonates (e.g. acac),³ 2-picolinate,⁴ acetylides,⁵ and N-heterocyclic carbenes.⁶ In these cases, the lowest-energy excited states normally involve primarily the metal and the cyclometallated ligand, with the co-ligands playing only a minor role. Only in a few instances, such as 8-hydroxy-quinolate, does the co-ligand participate significantly in the emissive excited state.⁷

Surprisingly, phosphorus based co-ligands remain relatively unexplored, despite having shown some promise,⁸ and we are unaware of any cyclometallated platinum(II) luminophore with phosphinine co-ligands. Phosphinines – the phosphorus analogues of pyridines – constitute an intriguing family of ligands owing to their ability to act as strong π -acceptors. Since their discovery by Märkl *et al.*,⁹ investigations into their coordination chemistry have essentially been limited to low valence transition metal carbonyl complexes.¹⁰ The tedious procedures to synthesise phosphinines and their inadequate stability to harsh reaction conditions have hampered the exploration of their coordination chemistry with many transition metals.¹¹ However we note that several important papers by Müller *et al.* have appeared recently dealing with the development of chelating phosphinine ligands in order prepare coordination compounds with transition metals in medium to high oxidation states such as Pd(II), Pt(II) and Ir(III).¹² Given the high affinity of soft Pt(II) metal centres for phosphorus, it is surprising that there are so few reports on the coordination chemistry of phosphinines with Pt(II),¹³ and no studies into the electronic excited states of such compounds.

We were intrigued to explore the coordination chemistry of the «Pt(N[^]C-ppy)⁺» moiety with the monodentate 2,6-diphenyl-4-methylphos-phorin (**L_p**) (Scheme 1), and to investigate the effect of such strongly π -acidic co-ligands on the excited-state properties. During the course of our work, an octahedral *tris-P[^]C*-cyclometallated iridium(III) complex was reported but the compound proved to be non-emissive even at low temperature, apparently due to efficient non-radiative decay processes.¹⁴ This is in stark contrast with the complex reported in this communication that

exhibits a phosphinine based phosphorescence for the first time in a metal complex.



Scheme 1 Synthetic strategy of complex [Pt(ppy)(**L_p**)₂]CF₃SO₃ (**1**) with **L_p**.

It proved possible to synthesise the target complex [Pt(ppy)(**L_p**)₂]CF₃SO₃ under very mild reaction conditions (Scheme 1). The first step involved chloride abstraction from compound [Pt(ppy)(μ -Cl)]₂ using silver triflate in acetone. The resulting solvate species [Pt(ppy)(acetone)₂]CF₃SO₃ was treated directly with just over two equivalents of **L_p**. After 2 hours at room temperature, the reaction was worked up and the novel complex [Pt(ppy)(**L_p**)₂]CF₃SO₃ (complex **1**) was isolated in high yield (see Supplementary Information for experimental details[†]). The mild reaction conditions employed are in stark contrast with the rather harsh synthetic protocols typically associated with reactions in which the chlorides are displaced,³⁻⁸ but are crucial in facilitating the introduction of the sensitive phosphinines into the coordination sphere.

Complex **1** was characterized by multinuclear NMR and IR spectroscopy, elemental analysis, and by a single crystal X-ray diffraction study.[†] The ³¹P{¹H} NMR spectrum is especially informative (Fig. 1). It exhibits two doublets at 157.7 ppm and 133.3 ppm, attributed to the chemically different phosphinine centres, with ¹⁹⁵Pt satellites of ¹J_{Pt-P} = 1760 Hz and ¹J_{Pt-P} = 4470 Hz respectively. *Cis*-P-P coupling (²J_{P-P} = 46 Hz) is also observed, unambiguously confirming the coordination of two **L_p** ligands through phosphorus to the Pt(II) centre in solution. The inequivalence of the phosphinine ligands is also evident in the ¹H NMR spectrum (Fig. S1[†]). ¹⁹F NMR and IR spectroscopy confirm the presence of the triflate anion.

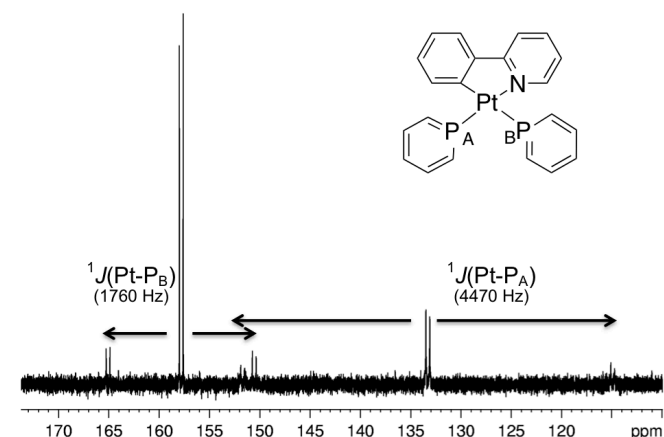


Fig. 1 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{Pt}(\text{ppy})(\text{L}_p)_2]\text{CF}_3\text{SO}_3$ (**1**) (the methyl and phenyl substituents as well as the triflate anion were omitted for clarity).

The solid-state structure of this first member of a novel type of phosphinine complexes was unequivocally ascertained by a single crystal X-ray diffraction study.¹⁵ The molecular structure in the crystal (Fig. 2) clearly shows that complex **1** has a distorted square planar geometry. The Pt(II) centre is coordinated by the phosphorus of two L_p ligands in a *cis*-fashion, and *trans* to the cyclometallated ppy ligand. Unfortunately, because of the serendipitous orientation of the ppy ligand, the positions of the nitrogen and cyclometallated carbon cannot be distinguished, prohibiting any deductions as to the Pt–N, Pt–P and Pt–C bond distances and angles.

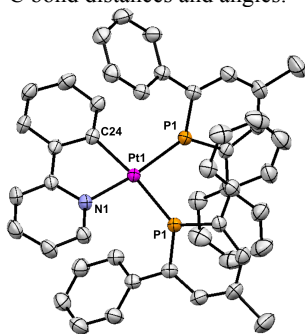


Fig. 2 View of the molecular structure of the cation in the crystal of complex **1**, exhibiting coordination of two phosphinine ligands to the “Pt(ppy)” unit. The H atoms and the triflate anion have been omitted for clarity.

The UV-visible absorption spectra of the phosphinine proligand L_p and of the Pt(II) complex **1** in dichloromethane solution at room temperature are shown in Fig. 3, with numerical data in Table 1. The spectrum of the proligand is dominated by an intense band centred at 278 nm ($\epsilon = 43700 \text{ M}^{-1}\text{cm}^{-1}$), accompanied by a shoulder at 312 nm, and a weak, low-energy tail, around 350 nm. There have been very few studies of the photophysical properties of phosphinines, but we note that the spectrum is similar to that of the related 2,6-thienyl-4-methylphosphinine,¹⁶ albeit somewhat blue-shifted. The intense bands can reasonably be attributed to $\pi\text{--}\pi^*$ transitions in the aromatic rings; lower-energy transitions would be expected in the thienyl derivative owing to the more electron-donating nature of thiophene compared to benzene. On the basis of TD DFT calculations, Mueller *et al.* assigned a similarly weak low-energy tail to a symmetry-forbidden $\text{S}_0\text{--}\text{S}_1$ transition.¹⁶ The absorption spectrum of the Pt(II) complex **1** shows an intense band at a similar value to L_p , presumably due to the superposition of intraligand transitions in the phosphinine with those of the phenylpyridine, but there are clearly now additional, moderately

intense bands in the 330–400 nm region (Fig. 3, Table 1). Bands in this region are typically found in $\text{Pt}(\text{N}^*\text{C})$ complexes (where N^*C represents a cyclometallated aryl-heterocycle such as phenylpyridine), due to charge-transfer transitions, normally from the metal / aryl ring to the heterocycle, according to theoretical calculations.^{1–8}

Table 1 Photophysical data for phosphinine L_p and complex **1**

	$\lambda_{\text{max}} / \text{nm}$ ($\epsilon / \text{M}^{-1}\text{cm}^{-1}$) ^a	$\lambda_{\text{lum}}^{\text{max}} / \text{nm}$ ^b	$\tau_{\text{lum}} / \mu\text{s}$ ^c
Proligand L_p	278 (43700), 312sh (17900), 352sh (1350)	405(F), 582(P)	-- ^c , 18700(P)
Complex 1	270 (54000), 332 (19300), 374sh (5220)	586	230

a Absorption data in CH_2Cl_2 at 298 K. *b* Emission data in diethyl ether / isopentane / ethanol (L_p) or CH_2Cl_2 (**1**) at 77 K; F and P indicate proposed assignment of fluorescence or phosphorescence to observed bands of L_p . *c* Fluorescence lifetime too short to be determined reliably.

Proligand L_p shows very weak fluorescence centred around 400 nm at room temperature in solution. In a frozen glass at 77 K, two emission bands are observed: a rather poorly-defined band in the 400–500 nm region, and a more intense band centred at 582 nm (Fig. 3, Table 1). The latter band is attributed to phosphorescence from a triplet state on the basis of its very long lifetime, $\tau_{\text{lum}} = 18.7 \text{ ms}$.[‡] These observations are similar to those of the earlier report mentioned above, where the weakness of fluorescence was attributed to the symmetry forbidden nature of the $\text{S}_1\text{--}\text{S}_0$ transition, whilst low-temperature phosphorescence, red-shifted compared to L_p to 607 nm, was also observed, with a lifetime of around 1 ms.

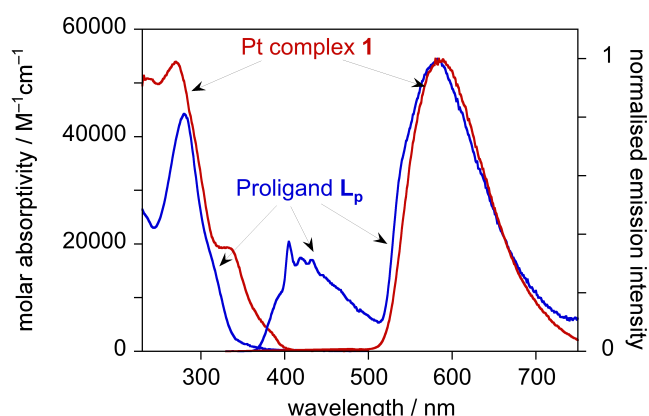


Fig. 3 UV-visible absorption spectra (in CH_2Cl_2 at 298 K) and photoluminescence spectra (in diethyl ether / isopentane / ethanol {2:2:1} and CH_2Cl_2 respectively) of L_p (blue lines) and complex **1** (red lines).

At room temperature, no significant emission can be detected from the platinum complex **1**. In contrast, intense emission is observed at 77 K (Fig. 3, Table 1). It is striking that the emission maximum under these conditions is very similar to that of the phosphorescence band displayed by L_p , but the lifetime is shorter by two orders of magnitude ($\tau_{\text{lum}} = 230 \mu\text{s}$) and there is no accompanying fluorescence band. These observations suggest that the emission in the complex emanates from an excited state that retains similar character to that of the free proligand L_p . Nevertheless, there must be sufficient influence of the metal through spin-orbit coupling to promote (i) $\text{S}\text{--}\text{T}$ intersystem crossing, such that fluorescence from the singlet state is quenched, and (ii) $\text{T}_1\text{--}\text{S}_0$ phosphorescence, such that the radiative rate constant is increased and the lifetime concomitantly shortened. At room temperature,

non-radiative decay pathways are evidently able to compete effectively with the slow radiative decay process, quenching the emission. This behaviour contrasts with that displayed by the majority of $\text{Pt}(\text{ppy})(\text{LL})^+$ and $\text{Pt}(\text{ppy})(\text{LX})$ complexes, where the excited state is typically based on the $\text{Pt}(\text{ppy})$ unit, with enough metal character that spin-orbit coupling pathways increase the radiative rate constant to the extent that luminescence is observable at room temperature, typically with a lifetime of around a microsecond.^{1–8} Support for this interpretation is provided by TD DFT calculations on complex **1**, carried out as described in the Supporting Information.[†] The T_1 excited state is predominantly HOMO→LUMO in character. The density difference plots for the T_1 excited state, calculated at the energy-minimised T_1 geometry, are shown in Fig. 4. They confirm that the excited state is localised largely on the phosphinine ligand that is *trans* to the metallated carbon. The metal makes only a minor contribution to the excited state, such that a rather long luminescence lifetime would be anticipated, as observed.

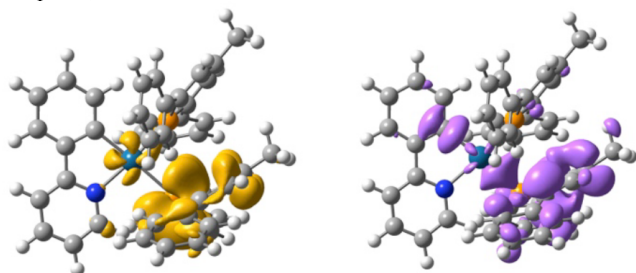


Fig. 4 Density difference plots for the lowest triplet excitation of complex **1** in CH_2Cl_2 , calculated at the optimised T_1 geometry, using PBE0 and the polarised continuum model for the solvent. Yellow and purple represent zones of depletion and augmentation of electron density in the T_1 excited state versus the S_0 ground state.

Electrochemical measurements can sometimes also provide insight into the location of the frontier orbitals. In the present instance, cyclic voltammetry of **1** in solution in CH_2Cl_2 reveals a well-defined, partially reversible reduction wave at -1.81 V versus the ferrocene/ferrocenium couple, anodically shifted compared to L_p ($E^{\text{red}} = -2.45$ V). This contrasts with the behaviour of related complexes such as $[\text{Pt}(\text{ppy})(\text{acac})]$, where reduction is not observed within the solvent accessible window, supporting the notion that the LUMO lies on the phosphinine. On the other hand, no clearly defined oxidations could be observed.

In summary, the first example of a cyclometallated platinum(II) complex incorporating phosphinine co-ligands has been described, in which the ligands are bound through phosphorus to a cyclometallated platinum centre. The complex is strongly luminescent at low temperature, from an excited state associated primarily with one of the phosphinine ligands. The study may open up further opportunities for introducing phosphinine ligands into novel metal complexes that display interesting physical properties.

Notes and references

^a UPMC Université Paris 06, Institut Parisien de Chimie Moléculaire (UMR 8232), 4 place Jussieu, 75252 Paris Cedex 05, France. Tel: (33)1-44-27-30-83; E-mail: jamal.moussa@upmc.fr; hani.amouri@upmc.fr

^b Department of Chemistry, Durham University, Durham, DH1 3LE, U.K. E-mail: j.a.g.williams@durham.ac.uk

[†] Electronic Supplementary Information (ESI) available: details of experimental procedure, NMR spectra, density functional theory calculations, and instrumentation for photophysical and electrochemical measurements. A CIF file containing crystallographic data of complex **1** is available at CCDC 982683. See DOI: 10.1039/b000000x/

[‡] The spectrum was independent of concentration over an order of magnitude range, ruling out the possibility that the low-energy band is due to aggregation.

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